
(12) **UK Patent Application** (19) **GB** (11) **2 105 346 A**

(21) Application No **8223643**

(22) Date of filing **17 Aug 1982**

(30) Priority data

(31) **56/131356**

57/070652

(32) **21 Aug 1981**

27 Apr 1982

(33) **Japan (JP)**

(43) Application published
23 Mar 1983

(51) **INT CL³**

C08F 8/36

(52) Domestic classification

C3J AN

C3P 202 203 210 220

222 302 322 330 FE

C3W 209 215 225

U1S 1350 C3J C3P

(56) Documents cited

GB 0959514

GB 0719685

US 4269943

(58) Field of search

C3J

C3P

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(54) **Process for producing cation
exchange resin**

(57) A cation exchange resin is
produced by (a) suspension
polymerizing a mixture of (1) styrene,
(2) divinylbenzene and (3) acrylic or

methacrylic acid or a C1—6 alkyl
ester of either acid, and (b) sulfonating
the copolymer particles.

The sulfonated particles are free of
cracks and do not cause brown color
in the eluate.

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SPECIFICATION

Process for producing cation exchange resin

The present invention relates to an advantageous process for producing a cation exchange resin which is industrially valuable.

5 In general, cation exchange resin is produced by sulfonating particles of copolymer of styrene and divinylbenzene. Since cation exchange resin having a large ion exchange capacity per unit weight is preferable, the sulfonation must be uniformly conducted throughout the entire polymer particles from surface to inside. However, the styrene-divinylbenzene copolymer particles have a disadvantage that the inside thereof does not easily undergo sulfonation.

10 A method comprising swelling the copolymer particles with as swelling agent an organic solvent such as nitrobenzene and then sulfonating the particles thus treated has been known for increasing the ion exchange capacity. However, the method has the following problems.

The first problem is that due to the use of a swelling agent, the number of treatment steps increases and further due to the presence of the swelling agent in a waste acid after sulfonation, the waste acid cannot be recycled for reuse, resulting in an economic disadvantage. In order to overcome this disadvantage, a copolymer including acrylonitrile in addition to styrene and divinylbenzene can be used and the sulfonation is carried out substantially in the absence of a swelling agent as described in, for example, Japanese Patent Publications 10343/1963 and 12602/1966. This method is preferred in that the sulfonation smoothly proceeds without the use of a swelling agent, but has another disadvantage in that a large number of cracks appear on the copolymer particles. A method in which sulfonation proceeds satisfactorily in the absence of a swelling agent has not yet been found.

The second problem is that the cation exchange resin obtained by the sulfonation is colored brown and during the use of the resin some of the colored component in the resin is dissolved in the treating solution, particularly when the resin is used after storage for a long period of time. The reason is believed to be that a portion of the coloring components formed at the sulfonation step changes into a water-soluble component during storage of the resin. No method is known to effectively overcome this second problem.

We have now found that the use of a copolymer comprising styrene, divinylbenzene and a specified third comonomer can overcome those problems.

30 Accordingly, the present invention provides a process of producing a cation exchange resin which comprises suspension polymerizing a monomeric mixture comprising (1) styrene, (2) divinylbenzene and (3) at least one compound selected from acrylic acid, methacrylic acid and lower alkyl esters of acrylic or methacrylic acid, having 1 to 6 carbon atoms in the alkyl moiety, and (b) sulfonating the resulting copolymer particles.

35 The copolymer particles which are a matrix of the cation exchange resin according to the present invention are a copolymer obtained by said suspension polymerization.

Preferred examples of component (3) are methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, acrylic acid, methyl acrylate and ethyl acrylate, and the amount of this component is preferably 2 to 20 mole %, more preferably 4 to 10 mole %, per mole of styrene. If the amount is too small, sulfonation of the resulting copolymer particles does not proceed smoothly and, on the contrary, if the amount is too large, exchange groups are not introduced due to decrease in the amount of styrene.

The amount of divinylbenzene used depends upon the desired degree of cross-linking of the copolymer and is generally 0.8 to 55 mole %, preferably 1.5 to 45 mole %, per mole of styrene.

45 It is novel in the production of cation exchange resin to use a copolymer containing acrylic acid, methacrylic acid or lower alkyl ester thereof as copolymer particles. It has been known in the production of anion exchange resin to use a copolymer containing methyl methacrylate, trimethyl propane trimethacrylate, acrylonitrile, isodecyl methacrylate, etc., as copolymer particles as described in, for example, U.S. Patent 4,207,398.

50 However, cation exchange resin and anion exchange resin are different in the production methods, treating conditions and the like and also have different properties. For example, in the production of anion exchange resin, acrylonitrile is used similarly to methyl methacrylate as disclosed in U.S. Patent 4,207,398. On the other hand, in the production of cation exchange resin, the use of acrylonitrile is not preferred, as is apparent from the data described hereinafter. This difference is due to the technical contents between anion exchange resin and cation exchange resin.

55 According to the present invention, the monomers (1) to (3) above are suspension polymerized. Water is generally used as a dispersing medium; the amount of water used is 1 to 10 times the total weight of the monomers.

60 Polyvinyl alcohol, carboxymethyl cellulose or the like may be as a dispersing agent. The amount of the dispersing agent is generally 0.1 to 5.0% by weight based on the total weight of the monomers.

Polymerization initiators which can be used are conventional materials such as benzoyl peroxide or azo type catalyst and the amount thereof is 0.01 to 15% by weight based on the total weight of the monomers.

The polymerization is generally carried out at the temperature of 50 to 90°C for 3 to 30 hours by,

for example, the following procedures: Predetermined amounts of water and dispersing agent are placed in a polymerization reactor, then monomers in which a polymerization initiator has been dissolved are added thereto with stirring, and the resulting oil-in-water suspension is subjected to a polymerization at a predetermined temperature while blowing nitrogen gas through the mixture.

5 Copolymer particles obtained by the suspension polymerization are crack-free beads having a particle diameter of usually 0.1 to 1.0 mm. The particles are then sulfonated to give the desired cation exchange resin. 5

Sulfonation is usually conducted by stirring the copolymer particles in 95 to 100 wt% sulfuric acid. The amount of the sulfuric acid used is generally 3 to 30 times the weight of the copolymer used.

10 The present invention includes a process wherein sulfonation is conducted substantially in the absence of a swelling agent and also a process wherein sulfonation is conducted in the presence of a swelling agent. In the case that the swelling agent is not used, there is a merit that the waste acid after the sulfonation does not contain an organic solvent therein and in the case that the swelling agent is used, there is another merit that the content of the coloring component in the resulting cation exchange resin is less. 10 15

The temperature of sulfonation is usually 50 to 150°C, preferably 90 to 110°C, when a swelling agent is used and usually 50 to 100°C, preferably 60 to 90°C, when a swelling agent is not used. When the temperature is too high in the case that the swelling agent is used, it is not possible to make the content of the coloring component in the resin satisfactorily low. The time required for sulfonation is generally 3 to 30 hours. 15 20

The swelling agent used is an organic solvent and the examples thereof are an aromatic hydrocarbon such as nitrobenzene, toluene or xylene; an aromatic halogenated hydrocarbon such as chlorobenzene or dichlorobenzene; an aliphatic halogenated hydrocarbon such as carbon tetrachloride or ethylene dichloride.

25 The swelling treatment of the copolymer particles is generally conducted by suspending the copolymer particles before sulfonation in a large excess of an organic solvent, followed by stirring at 50 to 100°C for 1 to 5 hours. 25

The copolymer particles after the sulfonation reaction are filtered and washed in conventional manner and then recovered after converting, if desired, from H-form to Na-form.

30 As described above, the production of the cation exchange resin using copolymer particles consisting essentially of specified components according to the present invention can provide the following advantages: 30

(1) Even when the sulfonation is conducted without a swelling agent, the resulting resin is not cracked, uniform sulfonation proceeds smoothly, and no organic solvent is contained in the resulting waste acid, and 35

(2) when the sulfonation is conducted using a swelling agent, coloring component in the resulting resin decreases. 35

Thus, the present invention can advantageously produce a cation exchange resin which is industrially valuable.

40 The present invention will now be explained in greater detail by reference to the following Examples and Comparison Examples. 40

EXAMPLES 1 TO 5 AND COMPARISON EXAMPLES 1 TO 2

45 A 3-liter flask equipped with a stirrer, a thermostat and a nitrogen gas inlet were charged with 2,000 g of water and 3.0 g of polyvinyl alcohol. Then, a mixture of 550 g of styrene, 80 g of divinylbenzene, a compound shown in Table 1 and 0.5 g of benzoyl peroxide were added to the flask. Polymerization was conducted at 80°C for 8 hours with stirring while blowing nitrogen gas. 45

Copolymer particles were recovered from the mixture obtained after polymerization. 100 g of copolymer particles were suspended in 650 g of 100% sulfuric acid and sulfonated at 100°C for 5 hours.

50 The ion exchanging capacity and ratio of broken particles during the sulfonation of the resulting cation exchange resins were measured and the results obtained are shown in Table 1 below. 50

TABLE 1

Example No.	Compound	Amount Added* ¹⁾ (mole%)	Ion Exchanging Capacity* ²⁾ (meq/g)	Ratio of Broken Particles* ³⁾ (%)
1	Ethyl acrylate	6	4.5	5
2	Ethyl acrylate	15	4.5	5
3	Methyl methacrylate	6	4.5	5
4	Ethyl methacrylate	5	4.5	5
5* ⁴⁾	Methacrylic acid	7	4.5	10
Comparison Example 1	—	—	2.0	80
Example 2	Acrylonitrile	6	4.5	80

Notes

*¹⁾ Mole% per mole of styrene*²⁾ Per 1 g of the resin*³⁾ The ratio of particles having cracks present in 100 resin particles*⁴⁾ The amount of benzoyl peroxide was 1.0 g.

EXAMPLES 6 TO 9

A 3-liter flask equipped with a stirrer, a thermostat and a nitrogen inlet was charged with 2,000 g of water and 3.0 g of polyvinyl alcohol. A mixture of 550 g of styrene, 80 g of divinylbenzene, a third monomer as shown in Table 2 and 0.5 g of benzoyl peroxide was added to the flask. The mixture was polymerized at 80°C for 8 hours with stirring while blowing nitrogen gas.

Copolymer particles were recovered from the mixture after polymerization. 100 g of the particles were stirred in a mixture of 50 g of a swelling agent shown in Table 2 and 300 ml of water at 80°C for 1 hour. The copolymer particles were recovered therefrom and then sulfonated in 500 ml of a 100% sulfuric acid at 80°C for 15 hours.

Sulfonated copolymer particles were filtered and washed ten times with 500 ml of water.

Measurement of ion exchanging capacity and an elution test of coloring component of the resulting cation exchange resin were conducted and the results obtained are given in Table 2 below.

TABLE 2

Example No.	Third Monomer		Swelling Agent Used	Sulfonation Temperature (°C)	Ion Exchanging Capacity (meq/g)	Elution Test** (APHA)
	Compound	Amount Added*				
6	Methacrylic acid	2.5	Nitrobenzene	80	4.52	20
7	Methacrylic acid	6.0	Nitrobenzene	80	4.42	20
8	Methyl methacrylate	2.5	Nitrobenzene	80	4.53	20
9	Ethyl methacrylate	2.5	Nitrobenzene	80	4.52	20

* Amount Used: Mole% per mole of styrene

** Elution Test: After storage in the air for 3 months, 50 g of resin was dipped in 200 ml of water at 60°C for 3 hours and the degree of coloration of the water was measured.

CLAIMS

1. A process of producing a cation exchange resin, which comprises (a) suspension polymerizing a monomeric mixture comprising (1) styrene, (2) divinylbenzene and (3) at least one compound selected from acrylic acid, methacrylic acid and alkyl esters thereof wherein the alkyl moiety has 1 to 6 carbon atoms, and (b) sulfonating the resulting copolymer particles. 5
2. A process as claimed in Claim 1, wherein the amount of the monomer (3) is 2 to 20 mole% per mole of styrene.
3. A process as claimed in Claim 1 or 2, wherein the amount of divinylbenzene is 0.8 to 55 mole% per mole of styrene.
- 10 4. A process as claimed in Claim 1, 2 or 3, wherein the copolymer particles have a particle diameter of 0.1 to 1.0 mm. 10
5. A process as claimed in any preceding claim, wherein the sulfonation is carried out using 95 to 100 wt% sulfuric acid.
- 15 6. A process as claimed in any preceding claim, wherein the sulfonation is carried out substantially in the absence of organic solvent as swelling agent. 15
7. A process as claimed in Claim 6, wherein the sulfonation temperature is 50 to 150°C.
8. A process as claimed in any of Claims 1 to 5, wherein the sulfonation is carried out substantially in the presence of a swelling agent consisting of organic solvent, at a temperature of 50 to 100°C.
- 20 9. A process as claimed in Claim 8, wherein the swelling agent is an aromatic hydrocarbon, aromatic halogenated hydrocarbon or aliphatic halogenated hydrocarbon. 20
10. A process as claimed in Claim 1, substantially as hereinbefore described with reference to any of Examples 1 to 9.
11. A cation exchange resin which has been produced by a process as claimed in any preceding claim.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office
25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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